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14. ABSTRACT

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants. A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

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Design of Energetic Ionic Liquids

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Abstract

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc. From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine—which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion. A hierarchy of computational approaches is employed, including atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed phase atomistic molecular dynamics simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ionic liquids based upon multiscale coarse graining techniques.

1. Introduction

The design of new high energy density materials, which are more efficient, reliable, and environmentally benign than existing rocket propellants, is a high DoD priority. The focus of this effort has been on the development of new propellants and energetic additives, including highly strained hydrocarbons, polynitrogen compounds, and advanced monopropellants. Some of the issues that must be addressed in theoretical efforts to design new energetic materials include an assessment of their energy content, their thermodynamic and kinetic stability, and the design of new synthetic routes to proposed new compounds that have not yet been synthesized.

A specific area of interest to the DoD is the discovery of a suitable replacement for hydrazine, a widely used monopropellant for low-thrust propulsion applications such as orbital maneuvering and satellite stationkeeping. The desire to replace hydrazine is motivated by several factors. Perhaps the most severe limitation of hydrazine is its carcinogenic nature and extreme respiratory and dermatological toxicity, with correspondingly large costs associated with controlling these environmental and toxicological hazards. Furthermore, the performance of hydrazine as a monopropellant is rather modest due to its relatively low density and specific impulse compared to a prototypical ionic monopropellant salt such as 4-amino-1,2,4-triazolium dinitramide. The replacement of hydrazine with more energetic, less hazardous energetic monopropellants is clearly needed.

A specific type of energetic material of current interest is derived from a broad class of compounds known generically as ionic liquids (ILs), which are chemical salts with unusually low melting points; e.g., below 100° C. The general interest in ILs has focused mainly on their use as environmentally benign ("green") solvents for a wide range of chemical reactions. Some of the properties of ILs which make them attractive as solvents include their low vapor pressure, large liquid ranges, and thermal stability. The interest in ILs as new monopropellants stems from several factors. For example, the properties of ILs, including their energy content, can be "tuned" through a judicious choice of component ions and their substituent. Furthermore, the virtually nonexistent vapor pressure of ILs greatly reduces the environmental and toxicological hazards due to respiratory and dermatological toxicity. Finally, the densities of ILs generally are significantly greater than those of conventional liquid monopropellants such as hydrazine.

Although there have been extensive experimental studies of chemical reactions in ILs, little has been done in the area of characterization of the fundamental chemical and physical properties of ILs. In particular, one of the most pressing needs in the broader area of IL development, and particularly in the design of energetic ILs, is the application of robust theoretical methods for the reliable prediction of IL heats of formation, synthesis routes, phase transitions, ion conformations, thermal stabilities, densities, and viscosities. The focus of this study is on the characterization, design, and synthesis of the next generation of monopropellants for rocket propulsion applications.

2. Computational Methods

An integrated approach utilizing multiple computational methods is used to predict and characterize the intrinsic and bulk properties of energetic ionic liquids. At the molecular level, highly accurate electronic structure methods are used to predict the fundamental properties of the ionic liquid components, including molecular structures, charge delocalization, heats of formation, and proton transfer reaction pathways and barriers. Geometries, electronic structures, and properties (including heats of formation) of the component ions are predicted using second-order perturbation theory (MP2, also known as MBPT(2)[1]), density functional theory (DFT)[2], coupled cluster theory (CCSD(T)[3]) and the "Gaussian-N" (GN)[4] methods. The Nuclear-Electronic Orbital (NEO)[5] approach is used for capturing the quantum dynamical effects of hydrogen bonding and proton transfer. The Fragment Molecular Orbital (FMO) method[6], which decomposes a large molecular system (e.g., a cluster, protein, liquid, zeolite, etc.) into small subunits (fragments) that are designed to both retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources, is used in studies of ion clusters. In addition, the complex spectrum of ionic liquid physical properties requires utilization of atomistic molecular dynamics and coarse-grained condensed phase simulations in order to obtain reliable predictions of many key bulk properties.

GAMESS,[7] the primary quantum chemistry code used in this study, is highly scalable. For example, the fixed-size parallel efficiency of the GAMESS TI-08 large test case (MP2 gradient, 898 atomic orbitals) on the Cray XT3 at the Engineer Research and Development Center (ERDC) DoD Supercomputing Resource Center is 75% on 1,024 cores (single core mode, relative to 64 cores) and 68% on 2,048 cores (dual core mode, relative to 256 cores).

The condensed phase molecular dynamics (MD) simulations were performed using the scalable LAMMPS classical MD code, which delivers a scaled-size parallel efficiency of approximately 90% on 8,192 cores on a Cray XT3 (see http://lammps.sandia.gov/bench.html)

3. Results and Discussion

Ionic Clusters: Since the processes of ignition and combustion of ILs take place in the gas phase, it is vitally important to determine the nature of ILs in the vapor phase. For example, do the species present in the vapor phase consist of individual ions, single ion pairs, neutrals, larger clusters of ions or neutrals, or a mix of these? Furthermore, the species present in the vapor phase are relevant to experimentally measured enthalpies of vaporization, which is a key property in determining the performance of ILs as chemical propellants.

Ionic liquids generally have negligible vapor pressures; nonetheless, it has been shown that some ILs can be distilled in vacuum with minimal thermal degradation. Recent photoionization experiments of IL vapors using a tunable light source have been performed to characterize the species present in the gas phase as well as to measure the enthalpies of vaporization.[8] To aid in the interpretation and confirmation of these and other similar experimental results, electronic structure calculations have been performed on the 1-ethyl-3-methylimidazolium bromide ($[emim^+][Br^-]$), 1-ethyl-3-methylimidazolium thiocyanamide ($[emim^+][SCN^-]$), N-butyl-N-methylpyrrolidinium dicyanamide ($([bmpyr^+][dca^-]$), and N-butyl-N-methylpyrrolidinium *bis*(trifluoromethylsulfonyl)imide ($[bmpyr^+][im^-]$) gas phase ion pairs. The geometries, interaction energies, and adiabatic ionization potentials (IPs) of the parent single ion pairs and fragments thereof were computed at the MP2/6-31+G(d,p)[9] and M06/aug-cc-pvtz[2,10] levels of theory.

Figure 1 is a notional energy diagram of the ionization and fragmentation pathways originating from the $[emim^+][Br^-]$ ion pair. This figure illustrates the relationship between the observed fragments and their appearance energies as a function of photon energy used in the photoionization step. Also shown in Figure 1 are the calculated and experimental adiabatic ionization potentials (IP) and appearance energies (AE) of the four primary fragments: ethylimidazole (EIM), methylimidazole (MIM), ethyl bromide (EtBr), and methyl bromide (MeBr). The calculated IPs and EAs are in good agreement with experiment, consistently within 0.1-0.2 eV of the observed values, and therefore lend strong support to the notion that the vapor phase of 1-ethyl-3-methylimidazolium bromide consists exclusively of single ion pairs. Figure 2 shows the optimized geometry of the $[emim^+][Br^0]$ cation complex, which is produced from photoionization of the $[emim^+][Br^-]$ ion pair. The calculated highest (singly) occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $[emim^+][Br^0]$ are also shown in Figure 2 and are qualitatively consistent with the observed fragmentation chemistry (i.e, the HOMO on neutral bromine atom interacting with the LUMO on the $emim^+$ ring, leading to fragmentation.)

4-Amino-1,2,4-triazolium dinitramide ion clusters: Previous studies of ionic liquids[11] have focused on the decomposition of ion pairs, providing insight into the chemistry of their ignition as high-energy fuels. The focus of this study, however, is to accurately describe larger systems beyond single anion−cation pairs. Recent work by Li et al.[12] has provided an accurate structure of two ion pairs (two cations and two anions), providing a greater understanding of the molecular structure and intermolecular interactions. The same system is modeled here, along with systems of three and four ion pairs, to illustrate the effectiveness of the FMO method in accurately describing complex molecular clusters, with the goal of modeling much larger systems in the future.

Two ionic liquid systems, 1,2,4-triazolium dinitramide and 4-amino-1,2,4-triazolium dinitramide, were studied using both *ab initio* MP2 and the MP2 implementation of the FMO method[13] with each ion chosen as a FMO fragment or monomer. Structures composed of tetramers (two cations and two anions) and hexamers (three cations and three anions) were optimized at the MP2/6-31+G(d) level of theory. FMO2-MP2 and FMO3-MP2 single-point energy calculations were then performed for comparison with the fully ab initio results. Excellent agreement between the FMO2/3 and MP2 results was observed, with errors of less than 1.5 (0.5) kcal/mol for FMO2-MP2 (FMO3-MP2). These studies have been extended to octamers (four cations and four anions), which have been optimized at the MP2/6-31++G(d,p) level and compared to FMO2-MP2 single-point energy calculations. As shown in Table 1, the error in the FMO2-MP2 energies of the octamers is less than 1 kcal/mol relative to the full MP2 result.

Another consideration for larger molecular systems is the computer time required. To illustrate the overall effectiveness of the FMO method in both providing accurate results and reducing computational requirements, timings were performed for the ionic liquid systems described above. Due to the fact that FMO2 is in good agreement with the ab initio results, only timings for FMO2 will be shown. However, it is noted here that because

the tetramers and hexamers examined here are small, the FMO3 timings for these systems do no exhibit any time savings relative to the full MP2 calculations. The benefit of using FMO3 is only seen with larger systems.[14] Timings were performed on a Cray XT4 supercomputer using AMD Opeteron64 processors running at 2.1 GHz, located at the ERDC DSRC in Vicksburg, Mississippi. Single-point MP2 energy calculations were performed using 8, 16, and 32 processors with both FMO2 and MP2 using the 6-31+G(d) basis set. As shown in Table 2, FMO2 requires approximately half of the computer time of a full MP2 calculation on the tetramers. With the increase in available processors, the overall time requirements are cut in half for both FMO2 and MP2, showing good scalability for both methods. With an increase in system size from ionic liquid tetramers to hexamers, the computer time required for a fully ab initio calculation increases more than 6 fold, while the FMO2 requirement only doubles. Therefore, the FMO2 cost savings relative to full MP2 is much greater than that observed for the tetramers. Again, scalability for both methods is very good for the hexamers, cutting the computational time in half when doubling the number of available CPUs. It is apparent that as the system size increases to larger ionic liquid clusters or as the basis set size increases (or both), the computational requirements for a fully ab initio calculation will rapidly and increasingly exceed those for FMO2. It may be that as the system size increases, the importance of three-body contributions to the interaction energy will also increase, requiring the use of FMO3. Future work will determine the importance of three-body terms in ionic liquid systems, as well as the ability of the FMO method to describe larger molecular clusters.

Alkyl side chain length and anion effects on ionic liquids/water mixtures: Since water is strongly solvated by many ionic liquids, large scale atomistic MD simulations were carried out to investigate the effects of alkyl side chain length and anion on dynamics and structure in imidazolium-based ionic liquids/water mixtures. [15] The results of density and molar volume profile from MD simulations are in good agreement with experimental results.[16] Increasing the alkyl side chain length (replacing butylmethylimidazolium ($BMIM^+$) with octylmethylimidazolium ($OMIM^+$)) significantly changes the cation aggregation behavior, especially at the high water concentration region. While $BMIM^+$ cations dissolve in water at high water mole fractions, the $OMIM^+$ cations form micelle-like structures as shown in Figure 3.[15] Stronger attraction between cations and anions in $[OMIM^+]BF_4^-$/water mixtures inhibits anion diffusion. The Cl^- anion has a stronger electrostatic interaction with other particles in the ionic liquids/water mixtures, thus replacing the BF_4^- anion with Cl^- also slows the diffusion of cations and water molecules. For all the ionic liquids/water mixtures studied, the diffusion coefficients of water and anions increase rapidly at water mole fractions above 0.8, indicating that the ion-dominated networks have broken down and given way to water-dominated networks. Similar behavior has also been observed in experimental NMR[17] studies on 1-ethyl-3-methylimidazolium-based ionic liquids.

At low water mole fractions, the water structure is dependent upon the strength of the water–anion attraction. Therefore, water molecules are less likely to form clusters in $[OMIM^+]Cl^-$/water mixtures than in $[OMIM^+]BF_4^-$/water mixtures at low concentrations. A visual inspection of the water clusters in $[BMIM^+]BF_4^-$/water mixtures reveals that the water clusters are connected mainly by hydrogen bonds. This result implies that the aggregation of other polar solvents in ionic liquids will likewise be affected by the choice of anion, and these findings may be of help in the design of liquid crystals and tunable ionic liquid solvents for chemical reactions.

The calculated structure factors are also found to provide guidance for future experimental measurements, as depicted in Figure 4.[15] The results correspond to experimental small- and wide-angle X-ray scattering (SWAXS) results.[18] The partial structure factor of the oxygen atoms from the MD simulation reveal that water contributes to the structure factor at Q= 20–30 nm^{-1} and both structure factors exhibit change at water mole fraction $X_w = 0.75$, indicating a local structure transformation.

The rotational correlation analysis of the MD simulations demonstrates that the ionic liquid cations have a noticeable impact on the water rotational motion. $BMIM^+$ exhibits greater interaction with water than does $OMIM^+$, causing the slower rotation of water when at $X_w > 0.61$. The slope change of the rotational correlation time in $[BMIM^+]BF_4^-$/water mixtures at $X_w = 0.75$ provides further evidence for the experimental suggestion[19] that, at this water concentration, the ion pair interaction becomes significantly weakened by the water molecules.

4. Summary and Conclusions

The structures, interaction energies, adiabatic ionization potentials, and appearance energies of the gas phase $[emim^+][Br^-]$ ion pair and its fragmentation products have been predicted using second order perturbation theory (MP2/6-31+G(d,p)). The calculated IPs and EAs are in good agreement with experimental photoionization data,

thus confirming the dominant species in the vapor phase of ethylmethylimidazolium bromide are single ion pairs. The calculated HOMO and LUMO of the cation complex $[emim^+][Br^0]$ resulting from the photoionization of $[emim^+][Br^-]$ are qualitatively consistent with the observed fragmentation channels.

The geometries of 1,2,4-triazolium dinitramide and 4-amino-1,2,4-triazolium dintramide ion cluster tetramers (2 cations and 2 anions) and hexamers (3 cations and 3 anions) were optimized at the MP2/6-31+G(d) level of theory. Similarly, octamers (4 cations and 4 anions) were optimized at the MP2/6-31++G(d,p) level. For the tetramers, FMO2-MP2 and FMO3-MP2 single point energies at the MP2/6-31+G(d) geometries reproduced the full MP2 energies to within 0.69 and 0.03 kcal/mol, respectively. For the hexamers, the corresponding absolute errors in the FMO2-MP2 and FMO3-MP2 total energies were 1.35 and 0.27 kcal/mol, respectively. For the octamers, the absolute errors in the FMO2-MP2 total energies were less than 1 kcal/mol. Timings on the ERDC Cray XT4 performed using 8, 16, and 32 processors show that FMO2-MP2 single point energies for the 4-amino-1,2,4-triazolium dinitramide tetramer require approximately half of the computer time for a full MP2 energy calculation. Furthermore, for the hexamers the computer time for full MP2 increases more than 6-fold whereas for FMO2 the required computer time only doubles.

Effects of alkyl side chain length and anion on dynamics and structure in ionic liquid/water mixtures have been investigated by large scale atomistic MD simulations. Replacing the $BMIM^+$ cation with $OMIM^+$ results in stronger aggregation of the cations and slower diffusion of the anions. Replacing the BF_4^- anion with Cl^- alters the water distribution at low water mole fractions and slows diffusion in the mixtures.

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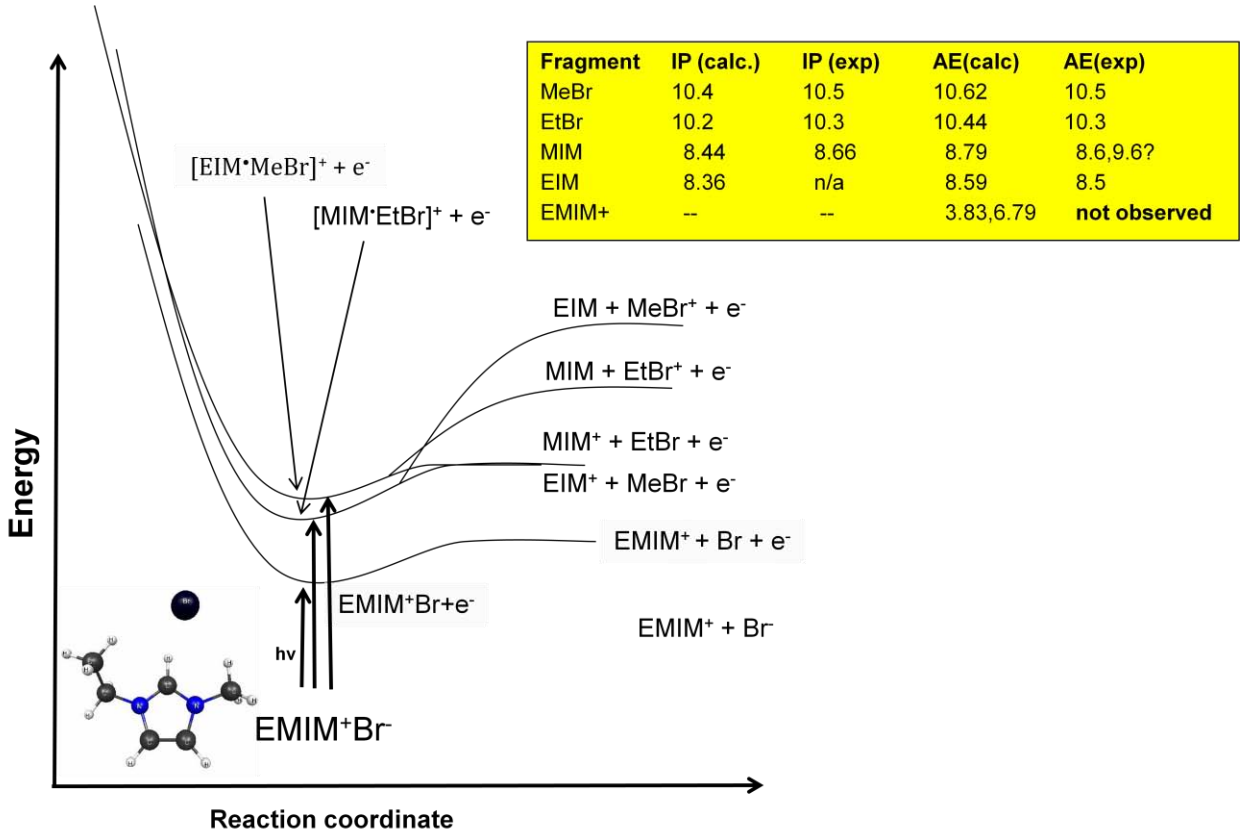
Table 1. FMO errors (kcal/mol) for tetramer, hexamer, and octamer ionic liquid clusters.

	Absolute Error (kcal/mol) 6-31+G(d)	
Tetramers	FMO2-MP2	FMO3-MP2
1,2,4-triazolium dinitramide	0.06	0.02
4-amino-1,2,4-triazolium dinitramide	0.69	0.03
Hexamers		
1,2,4-triazolium dinitramide	0.32	0.07
4-amino-1,2,4-triazolium dinitramide	1.35	0.27
Octamers	6-31++G(d)	
1,2,4-triazolium dinitramide	0.67	
4-amino-1,2,4-triazolium dinitramide	0.74	

Table 2. Timings for ionic liquid clusters performed on a Cray XT4 with 2.1GHz AMD Opteron64 processors. Each node contains a 4-core CPU and 8 GB of RAM.

		Timing (minutes) 6-31+G(d)	
Tetramer	# CPUs	FMO2-MP2	MP2
4-amino-1,2,4-triazolium dinitramide	8	12.2	28.4
	16	6.4	14.7
	32	3.5	7.3
Hexamer			
4-amino-1,2,4-triazolium dinitramide	8	24.0	172.1
	16	12.5	83.9
	32	6.8	42.8



Fragment	IP (calc.)	IP (exp)	AE(calc)	AE(exp)
MeBr	10.4	10.5	10.62	10.5
EtBr	10.2	10.3	10.44	10.3
MIM	8.44	8.66	8.79	8.6,9.6?
EIM	8.36	n/a	8.59	8.5
EMIM+	--	--	3.83,6.79	**not observed**

Figure 1. Energy diagram of the ionization and fragmentation channels of the [emim$^+$][Br$^-$]) ion pair, as a function of photon energy (not to scale). Calculated MP2/6-31+G(d,p) and experimental adiabatic ionization potentials (IP) and appearance energies (AE) are summarized in the upper right panel.

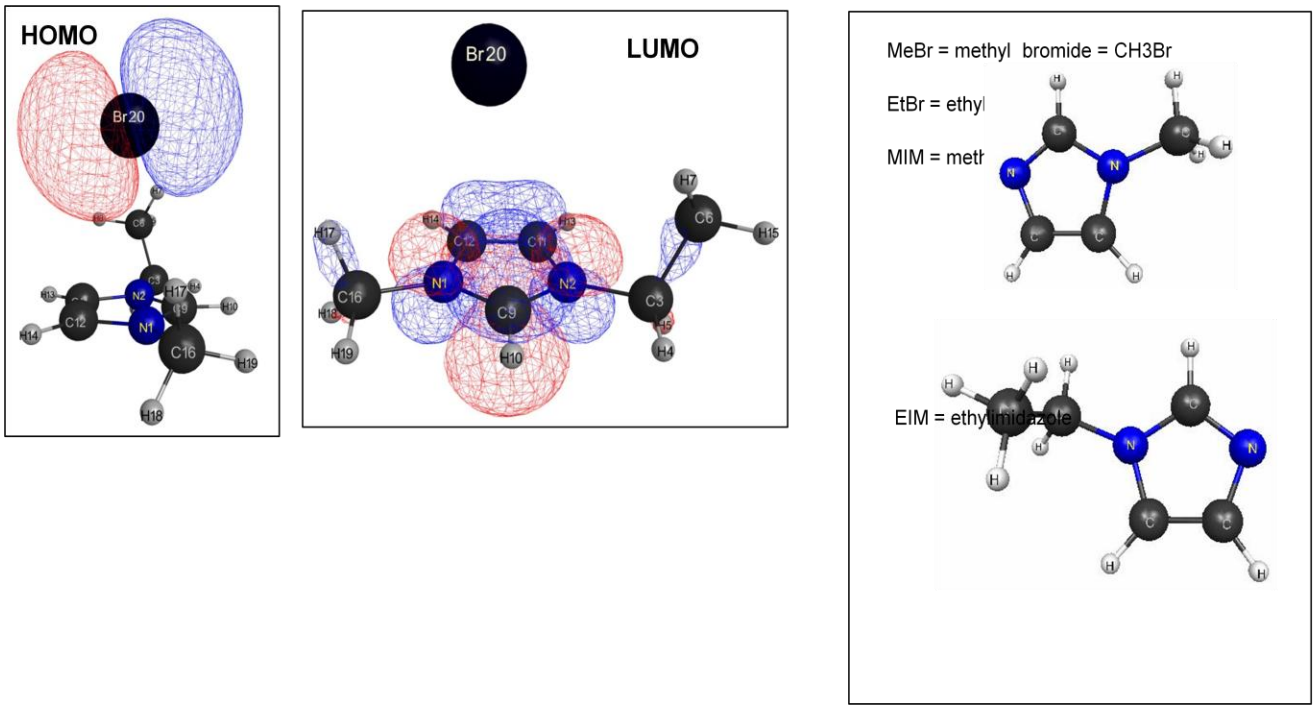


Figure 2. MP2/6-31+G(d,p) geometries of the [emim^{+}][Br^{0}] ion complex (left and middle panels). Also shown is the highest (singly) occupied molecular orbital (HOMO, left panel) and the lowest unoccupied molecular orbital (LUMO, middle panel) of [emim^{+}][Br^{0}]. Structures of the methylimidazole and ethylimidazole neutral fragments are shown in the panel on the right.

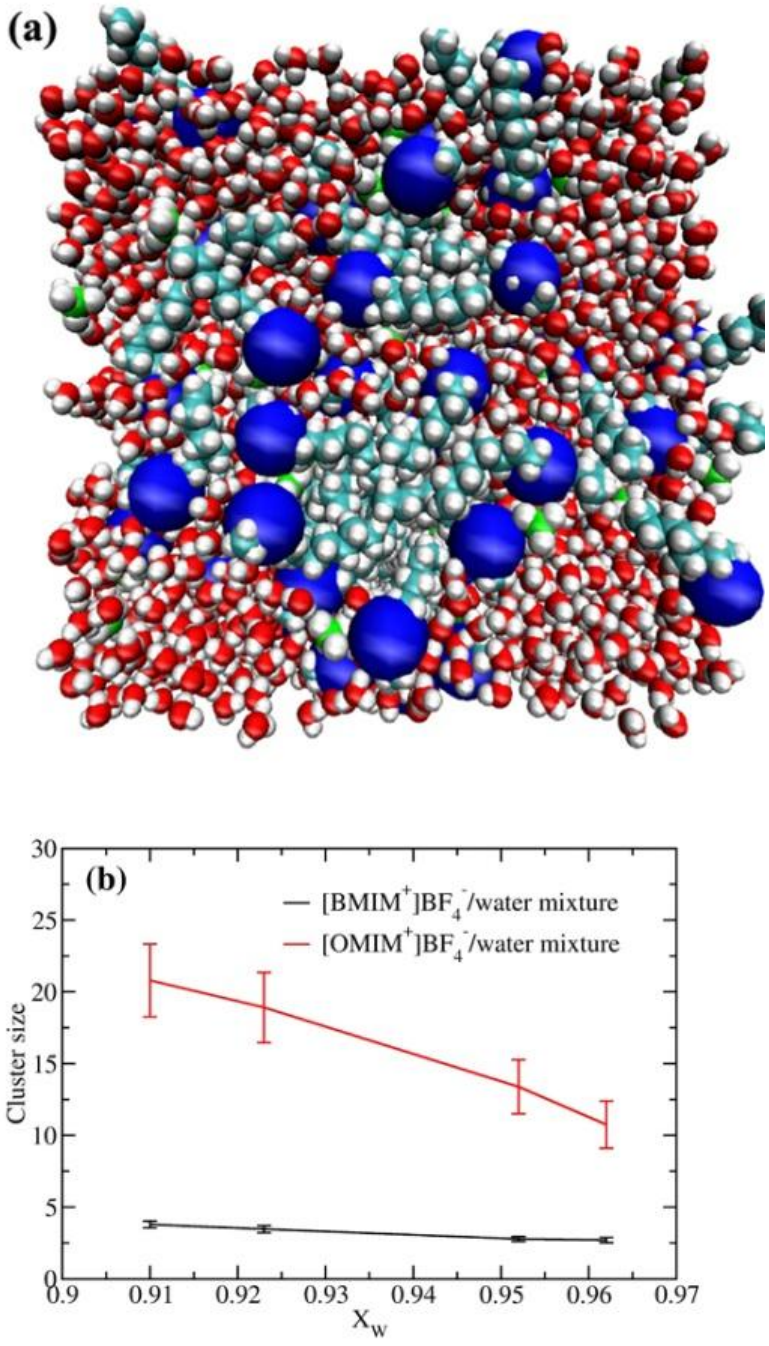


Figure 3. (a) Micelle-like structures observed in an $[OMIM^+]BF_4^-$/water mixture at water mole fraction 0.9615; O, B and C atoms are shown in the red, green and cyan spheres. The white spheres are either F or H atoms (depending upon their respective attachment to boron or oxygen). The large blue sphere represents imidazolium ring. (b) The average sizes of cation clusters observed in $[BMIM^+]BF_4^-$ and $[OMIM^+]BF_4^-$/water mixtures.

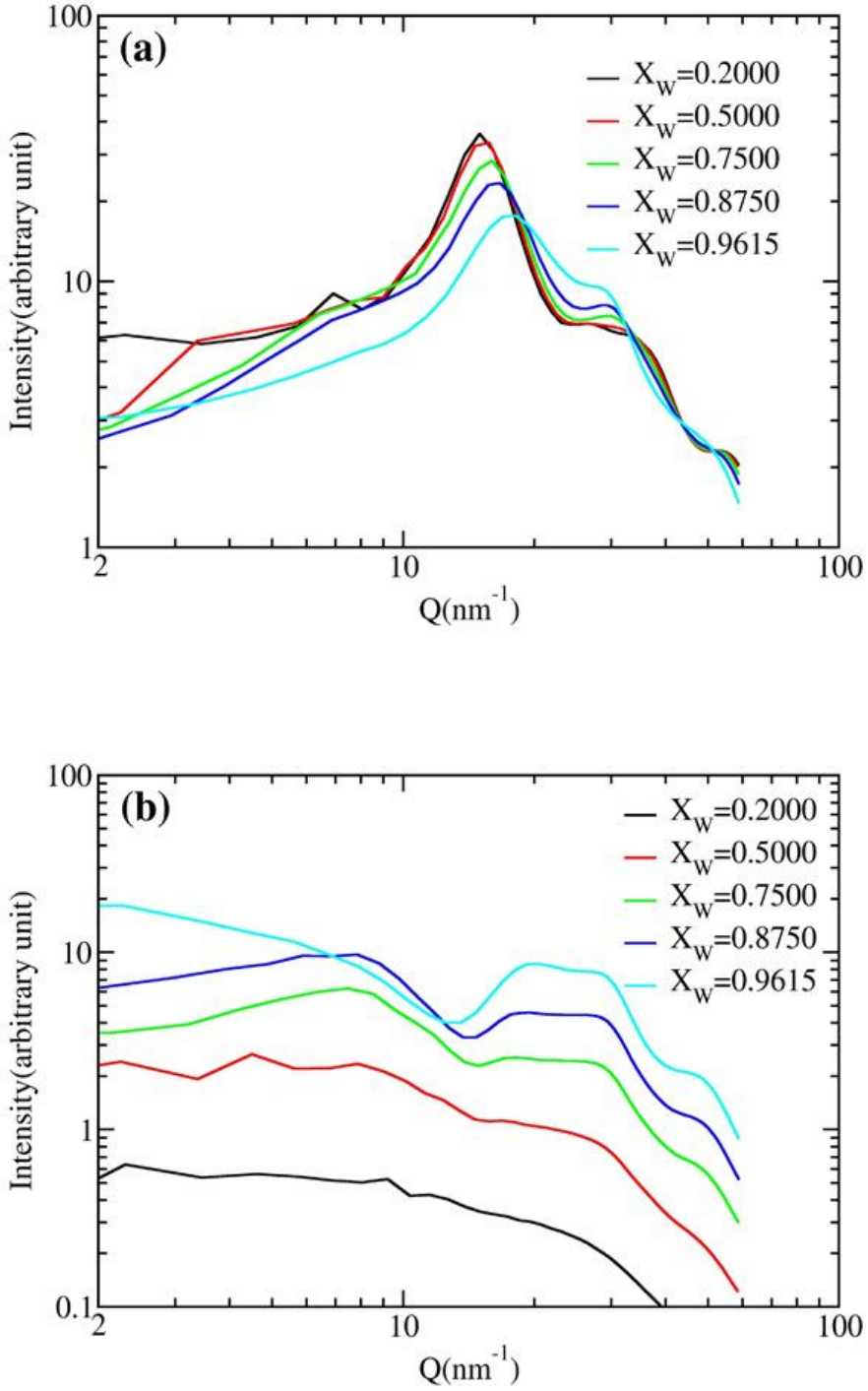


Figure 4. (a) Structure factors of [BMIM$^+$]BF$_4^-$/water mixtures at different water mole fractions(X_w); (b) Partial structure factor of oxygen atoms in the [BMIM$^+$]BF$_4^-$/water mixtures.